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Sediment oxygen demand during the winter in the Athabasca River and the Wapiti-Smoky River system, 1990

CANADIANA

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SUMMARY

In recent years interest has grown in the oxygen balance of the Athabasca River and Peace River systems because of proposed and expanding pulp mill and forestry related projects on these rivers. Sediment oxygen demand (SOD) is an important variable in the oxygen balance of rivers, in particular during the winter under low flow and extensive ice-cover. In 1989, a method to measure SOD *in situ* was developed and used to measure winter SOD rates in the Athabasca River. The main objectives of the 1990 study were to determine if SOD rates increased over the winter and to determine the longitudinal trend of SOD in the Athabasca River and the Wapiti-Smoky River system.

The stainless steel chambers developed in 1989 were used to measure SOD on the Athabasca River and the Wapiti-Smoky River system during January-March, 1990. For each river system, one 'control' site was upstream of the existing pulp mills at Whitecourt and Grande Prairie and the next site was immediately downstream of the pulp mill effluent. Other sites for the Athabasca River were: Blue Ridge, Fort Assiniboine, and Smith, and for the Wapiti-Smoky River system sites were: the mouth of the Wapiti River, Bezanson, and Watino. For the 1989 results, potential errors were identified which may have caused the SOD rates to be underestimated. For the 1990 study, a number of improvements were made but the SOD rates may still be underestimated, because of reduced mixing of water in the chamber and reduced velocity at the substratum-water interface.

For the Athabasca River, there was an increase in SOD over the winter but for the Wapiti-Smoky River system, a build-up of SOD over the winter was not

evident. This is because in March for the Wapiti River, the SOD appears to have been reduced due to erosion of the river bed caused by flooding. The winter increase of SOD downstream of the effluents is probably due to the accumulation of organic material which in turn would result in an increase of the benthic biomass and respiration. Presumably, in spring or during high river flow, scouring of the river bed reduces benthic deposits and biomass, thereby lowering SOD. At the 'control' sites the SOD was close to zero throughout the winter.

For both river systems, there was a clear longitudinal trend in SOD rates in 1990 and also, for 1989 in the Athabasca River. For both years including all study sites, the lowest SOD rates were measured at the 'control' sites and the highest SOD rates were found at the sites immediately downstream of the pulp mill and municipal effluents. The Millar Western Ltd. mill and the Whitecourt municipal effluent appeared to have a greater effect on the SOD in the Athabasca River than the Procter and Gamble Cellulose Ltd. mill effluent and the Grande Prairie municipal effluent in the Wapiti-Smoky River system. The SOD rates were higher and the SOD remained high further downstream in the Athabasca River than in the Wapiti-Smoky River system. The apparent difference in SOD between the Athabasca River and the Wapiti-Smoky River system may be due to differences in the type of pulp mill and the effluent.

For the Athabasca River and the Wapiti-Smoky River system, evidence was found to indicate that percent organic content of fine sediment and SOD were directly related. However, SOD was not directly related to the percent organic content of the epilithic sediment or the gravel and sand bottom samples of the rivers in this study.

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1. INTRODUCTION

Sediment oxygen demand (SOD) is an important variable in the oxygen balance of river systems. The SOD is particularily important during the winter when rivers in Alberta are ice-covered and reaeration from the atmosphere is reduced or does not occur. Interest in the winter oxygen balance of the Athabasca River and Peace River system has grown in recent years because of proposed pulp mill projects.

This study is part of the programs conducted by Alberta Environment to determine the dynamics and the importance of the principal components of the oxygen balance of the Athabasca and the Wapiti-Smoky Rivers during the winter. The 1990 winter study is a continuation of work conducted on SOD in 1989. During the winter of 1989, a method to measure SOD was developed and used at five locations between Hinton and Fort Assiniboine on the Athabasca River (Casey and Noton 1989).

The principal objective of this study was to use the method developed in 1989 to obtain additional measurements of SOD in the Athabasca River and to obtain measurements for the Wapiti-Smoky River system. Some modifications to the method for measuring SOD were made in 1990 to reduce potential errors in calculating the SOD rates. This study was designed to determine the change in SOD rates (1) over the incubation period when chambers were in situ, (2) during the winter and (3) to characterize the longitudinal trend of SOD on the Athabasca

River and the Wapiti-Smoky River system.

2. DESCRIPTION OF STUDY SITES

Ten study sites were located on the Athabasca River and the Wapiti-Smoky River system, upstream and downstream of existing pulp mills (Tables 1 and 2). Water quality data and other relevant information for some of these sites may be obtained in reports by Hamilton et al. (1985), Noton and Shaw (1989), and Noton et al. (1989).

2.1 Athabasca River

Five locations were sampled: Windfall bridge, Whitecourt, Blue Ridge, Fort Assiniboine, and Smith (Figure 1). The sites at Windfall bridge, Whitecourt and Fort Assiniboine were close to sites used in the 1989 study. All of the sites were ice-covered except at Whitecourt where most of the river was open water during the winter. The Whitecourt site was located about 1 km downstream of the Millar Western Ltd. mill effluent and upstream of the Whitecourt sewage effluent.

The main substratum at the study sites was a pebble-cobble mixture. However, at Blue Ridge and Fort Assiniboine most of the rocks were covered by a layer of fine sediment (Table 1).

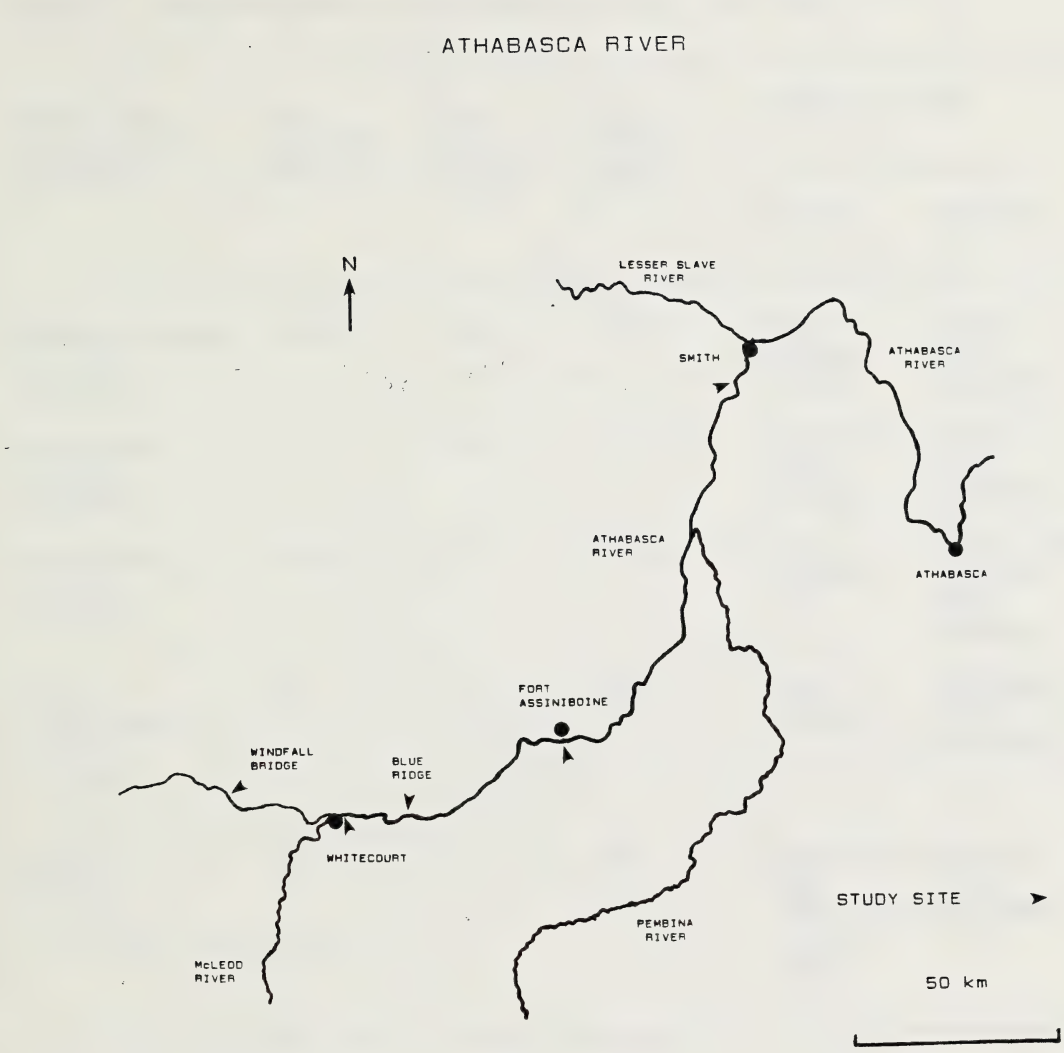

Figure 1. Study sites on the Athabasca River.

Table 1. Characteristics of the study sites for the Athabasca River.

Study Site, Latitude and Longitude	Ice Thickness (cm)	Mean Water Velocity (cm/s)	Mean Water Depth (cm)	Substratum Cover	
				Growth	Deposits
Windfall bridge 54 12'N, 116 3'W	82-100	0-26	58-75	Small amount, patchy	Patchy fine sediment
Whitecourt 54 9'N, 115 40'W	---	29-43	44-72	Gelatinous cover, abundant	Patchy fine sediment
Blue Ridge 54 9'N, 115 23'W	72-76	0-9	72-84	None visible	Patchy and abundant fine sediment
Fort Assiniboine 54 19'N, 114 46'W	67	7	71	None visible	Abundant fine sediment
Smith 55 4'N, 114 5'W	46	5	68	Macrophytic and encrusting algae, common	Patchy fine sediment

2.2 Wapiti-Smoky River system

Five locations were sampled: Wapiti River at Highway 40, about 2.5 km downstream of the Procter and Gamble (P & G) Cellulose Ltd. mill, and at the mouth, Smoky River at Bezanson and Watino (Figure 2). All of the sites were ice-covered except downstream of the Procter and Gamble mill. The Grande Prairie sewage effluent was located on the Wapiti River downstream of the site at the Highway 40 bridge on the Wapiti River and upstream of the Procter and Gamble effluents.

The most abundant substratum at the study sites was a cobble-pebble mixture, and fine sediment was also abundant downstream of the Procter and Gamble mill and at Bezanson (Table 2).

3. MATERIALS AND METHODS

The materials and methods used were similar to those used in the 1989 study (Casey and Noton 1989). The main methods are reviewed here with some minor changes included.

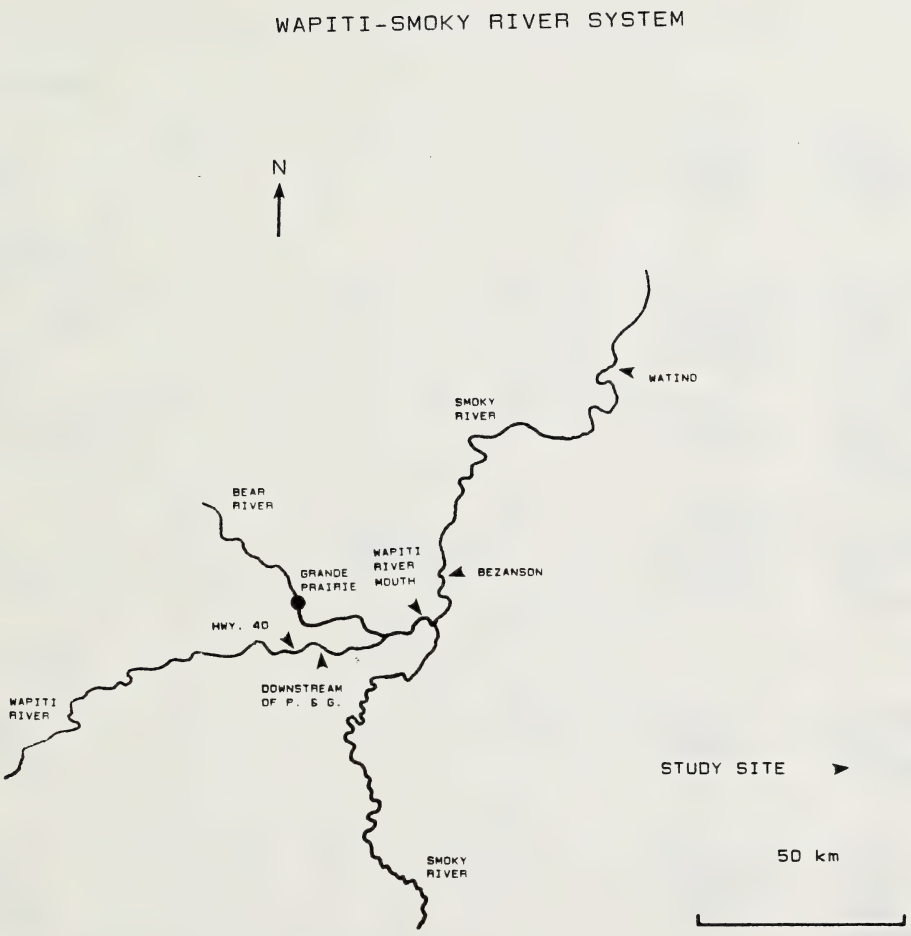

Figure 2. Study sites on the Wapiti-Smoky River system.

Table 2. Characteristics of the study sites for the Wapiti-Smoky River system.

Study Site, Latitude and Longitude	Ice Thickness (cm)	Mean Water Velocity (cm/s)	Mean Water Depth (cm)	Substratum Cover	
				Growth	Deposits
Wapiti River:					
Hwy. 40 55 4'N, 118 48'W	69-70	2-8	81-83	Small amount, patchy	Patchy fine sediment
Downstream of P&G(2 sites)* 55 4'N, 118 37'W Site 1: main channel	---	44**	66	Encrusting algae, abundant	Patchy fine sediment
55 4'N, 118 37'W Site 2: back-water	---	---	46	None visible	Abundant fine sediment
Mouth 55 8'N, 118 19'W,	54	Very fast**	58	Encrusting algae, common	$\leq$ 2 cm cover of fine sediment
Smoky River:					
Bezanson 55 14'N, 118 15'W	78	4	72	None visible	Abundant fine sediment
Watino 55 42'N, 117 37'W	79	7	74	Small amount, patchy	Light cover of fine sediment

* 2.5 km downstream of the Procter and Gamble Cellulose Ltd. mill effluent diffuser

** During sampling in March, water velocity was very fast but velocity was not measured

3.1 Field techniques

3.1.1 SOD chambers

As in 1989, both 'open' and 'closed' stainless steel chambers were used. Open chambers had an open base so that the chamber could be placed on the substratum. For closed chambers, the substratum had to be placed in the chamber. The type of chamber used depended on the substratum type and whether it was possible to obtain a seal between the substratum and the chamber. A closed chamber and the apparatus used to extract the water samples for analysis of dissolved oxygen are shown in Figure 3.

3.1.2 Use and positioning of the chamber

Minimum disturbance was caused to the substratum when using the open chambers. The chamber was simply placed on the substratum and pushed into the fine sediment to a depth of about 11 cm. At some locations where open chambers were used, closed chambers were also used to determine if disturbance to the sediment altered the rate of SOD. When using closed chambers under these conditions the fine sediment was placed in the chambers using a shovel with as little disturbance of the sediment as could be managed. At the sites with fine sediment, the sediment was observed to be layered and the sediment was placed in the chamber with the same orientation as in the river bed.

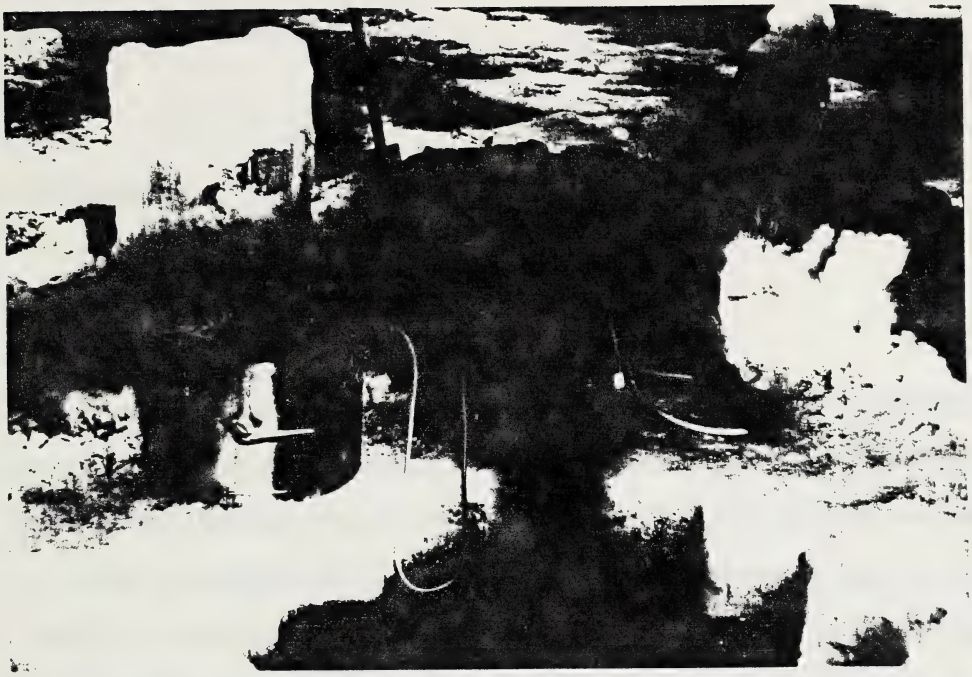

Figure 3. Sediment oxygen demand (closed) chamber and the water sampling apparatus. A weighted pipe was used to keep the apparatus, except the hand-pump, submerged to prevent water freezing in the tubing.

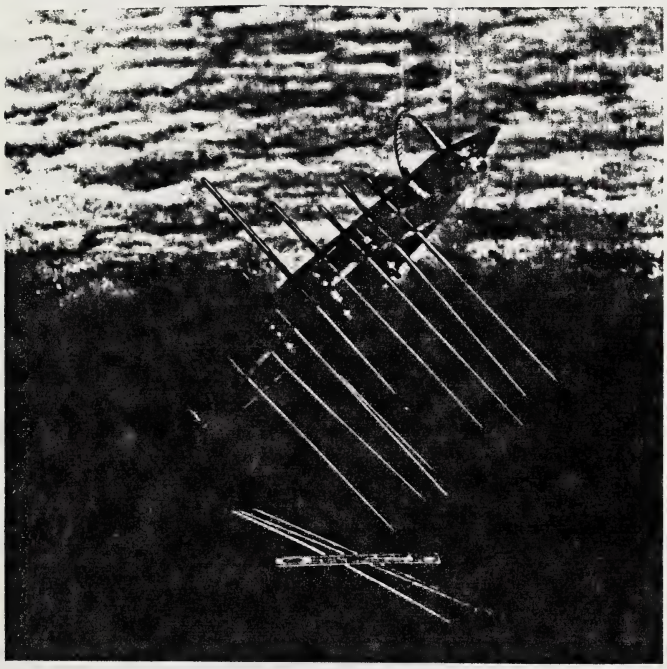

Figure 4. Modified depth-profile measuring device. A second Plexiglas plate was added to the apparatus used in the 1989 study to hold the rods perpendicular to the substratum in the chamber.

3.1.3 Measurements

3.1.3.1 Dissolved oxygen

Dissolved oxygen (DO) was measured by the azide-Winkler method (NAQUADAT no. 08101L), modified by sampling only 100 ml of water and using dilute reagents so as to maintain titration accuracy and precision. This modification was made so as to reduce a potential error which may have underestimated the 1989 SOD rates. When the chamber water is extracted for DO analysis, river water replaces the water in the chamber, thereby diluting chamber water and usually increasing the DO concentration in the chamber. Therefore, when a smaller sample is taken from the chamber the DO in the river water would have less of an effect on the DO in the chamber.

Exchange with river water was also reduced by measuring conductivity in the excess water extracted for the DO analysis instead of using the conductivity probe in the chamber *in situ*. In 1989 when the conductivity probe was used in the chamber a porthole had to be kept open permitting interchange of water.

3.1.3.2 Use of control chamber

At all sites in 1990, water column BOD rates were measured using control chambers, i.e. chambers containing water and no substratum. In 1989 for some study sites, a sealed dark, 300 ml BOD bottle was used instead of a control chamber. Use of the BOD bottles most likely resulted in overestimating the

oxygen demand of the water column, thus causing an underestimate of the SOD rates.

3.1.3.3 Volume of chamber

The volume of the chambers was measured in 1989 using a depth-profile measuring device. For 1990, this instrument was improved by attaching a second Plexiglas sheet to the original plate with a 1 cm gap between the plates (Figure 4). Thus when the depth rods were inserted through the Plexiglas plates, the rods were held more rigid and perpendicular to the substratum. When only one Plexiglas plate was used there was a tendency for the rod to rest on the substratum at a slight angle to the perpendicular. In 1989 this may have resulted in the volume of the chamber being slightly overestimated.

3.1.3.4 Other pertinent variables

The water seal in each chamber was measured using a solution of NaCl similar to the 1989 study. Other factors including river velocity and depth, ice thickness, and substratum characteristics were recorded at each site. For each chamber, the velocity of the water vane and the water depth above the vane were measured.

Scrapes of epilithic sediment and bottom sediment samples were taken in the chambers. The scrapes of material on the rock surface were taken from within a known area, as in 1989. Where fine sediment was abundant, a sample was taken of about 100 cm^3 from the top 2-3 cm depth of the sediment. For sites where it

was not possible to obtain a scrape of the epilithic sediment or where bottom sediment was scarce, about 100 cm^3 of material which was typically gravel and sand) was sampled from the bottom of each SOD chamber. The percent organic content of the samples was estimated by loss on ignition as in the 1989 study (Casey and Noton 1989).

4. RESULTS AND DISCUSSION

4.1 Evaluation of techniques

The changes to the methods used for the 1990 study resulted in improvements in the calculation of the SOD rates. These changes and relevant factors identified in last years study are reviewed here. More detailed discussion of the techniques are included with the 1989 study results (Casey and Noton 1989).

4.1.1 Dissolved oxygen measurement

Each time DO was measured, duplicate samples were taken and analysed. The DO in the duplicates was generally the same or there was a difference of about 0.10 mgO_2/L. Thus the interchange in water between the river and the chamber had little if any measurable effect on the DO levels recorded.

In a separate study in February 1990, the effect of the concentration of a kraft pulp mill effluent on the azide-Winkler method was examined. The pulp mill effluent used was from the Procter and Gamble mill at Grande Prairie. With increasing amounts of mill effluent in the water, increasing negative

interference in the azide-Winkler method was observed such that for river water containing 4 % effluent, similar to the 1990 conditions in the Wapiti River at the site downstream of the mill, a negative error of about 0.5 mg/L was estimated (L. Noton, Alberta Environment, pers. comm.). Although this may have influenced the measured DO, it seems that the SOD measurements should be valid since they are based on the change in DO and also because the changes were greater than the estimated negative error (Appendix 2).

4.1.2 Oxygen demand of the water column

After incubation, the change in DO in the control chambers was generally small, relative to the DO change in the chambers containing substratum (Appendices 1 and 2). The change in DO in the control chambers for all sites in the 1990 study ranged from 0.00 to 0.50 mgO_2/L, and averaged 0.19 mgO_2/L (n=25).

Similar to the results of the 1989 study, the DO in the control chambers increased in some cases instead of decreasing (Appendices 1 and 2). This increase in DO in the controls is considered to be a measurement error associated with the precision of the Winkler procedure. However, since the DO in the chambers containing the substratum was corrected using the DO change in the control chambers, a negative SOD rate was obtained in some cases. Negative SOD rates were obtained at Windfall bridge and Highway 40 on the Wapiti River (the two 'control' sites above municipal and mill effluents) where the change in DO in the chambers containing the substratum was low. In 1989 negative SOD rates were also obtained for Windfall bridge. In both years, such negative rates are

not likely significantly different from zero.

4.1.3 Volume of chamber

For sites where fine sediment was abundant, the depth-profile device was used, except at site 2 downstream of the Procter and Gamble mill. The depth to which the depth-profile rods sank into the fine sediment was accounted for by measuring the mark left by the sediment on the rods. At site 2 downstream of Procter and Gamble, turbidity of the water was high and it was not possible to use the depth-profile device. A meter ruler was used instead. Using the ruler, measurements were taken around the inside edge and at intervals across the surface of the substratum in the chamber. Both methods were considered accurate in determining the volume of the chambers.

4.1.4 Velocity and mixing of water

Water velocity beside the chambers *in situ* and the velocity of the water vane on the chambers was recorded to determine the relationship between the velocity of water in the river and in the chamber. Similar to the results for the 1989 study, the 1990 results demonstrated that the water vanes were often stationary when there was a measurable velocity in the river (Tables 3 and 4). This was most likely due to ice-cover and the position of the water vane relative to where the velocity of the river water was measured. At ice-covered sites, the velocity of the river was measured mid-way between the river bed and the bottom of the ice. However, the water vane was often located above the level of the bottom of the ice.

Table 3. Mean number and range of revolutions of the water vane and the water velocity for each group of chambers and study site on the Athabasca River. Number of measurements per group used to calculate the mean is shown in parentheses.

Study Site	Date (d.m.y.)	Revolutions per 30 s		Water Velocity (cm/s)	
		Mean	Range	Mean	Range
Windfall bridge	09.01.90	0.4(4)	0.0-1.75	26(4)	11-52
	09.02.90	0.0(4)	---	0(4)	
	09.03.90	0.0(4)	---	10(4)	5-19
Whitecourt	16.01.90	6.6(4)	5.5-7.5	43(4)	30-58
	08.02.90	6.0(4)	4.0-6.75	38(4)	24-45
	06.03.90	6.1(4)	4.75-6.75	29(4)	23-34
Blue Ridge	14.02.90	0.0(2)	---	0(2)	---
	11.03.90	0.0(4)	---	9(4)	3-18
Fort Assiniboine	13.03.90	0.0(4)	---	7(4)	5-8
Smith	14.03.90	0.0(4)	---	5(4)	3-5

Table 4. Mean number and range of revolutions of the water vane and the water velocity for each group of chambers and study site on the Wapiti-Smoky River system. Number of measurements per group used to calculate the mean is shown in parentheses.

Study Site	Date (d.m.y.)	Revolutions per 30 s		Water Velocity (cm/s)	
		Mean	Range	Mean	Range
Wapiti River:					
Hwy. 40	28.01.90	0.5(4)	0.0-1.75	3(2)	1-4
	27.02.90	0.0(4)	---	8(2)	8-8
Downstream of P&G*:					
Site 1	24.02.90	6.5(4)	5.0-7.25	44(4)	38-50
Site 1	22.03.90	Very fast**	---	Very fast**	---
Mouth	22.03.90	Very fast**	---	Very fast**	---
Smoky River:					
Bezanson	28.02.90	0.0(6)	---	4(2)	2-5
Watino	25.02.90	0.0(4)	---	8(2)	6-9

* Procter and Gamble Cellulose Ltd. mill effluent

** During sampling in March, water velocity was very fast but velocity was not measured

4.1.4 Summary

Modifications to the methods used in the 1990 study reduced potential errors identified in the 1989 results. The changes include taking a smaller water sample from the SOD chambers to calculate DO, using a control chamber at all sites and for all dates, and improving the design of the depth-profile device to obtain a more accurate measure of the volume of chambers. All of these factors increased the accuracy of the SOD rates. However, factors which may cause the SOD rates to be underestimated in this study include the use of an SOD chamber versus obtaining the oxygen balance using a respiration tunnel *in situ* (e.g. James 1974), reduced mixing of water in the chamber and reduced water velocity at the substratum-water interface (for further discussion see Casey and Noton 1989).

4.2 General findings

4.2.1 Change in SOD during the incubation period

4.2.1.1 Athabasca River

In January, three closed chambers were left *in situ* for 95 and 115 h at Windfall bridge and Whitecourt, respectively (Table 5). During these incubation periods, SOD rates were measured 4 times at each site (Table 6). The SOD rates for Whitecourt remained stable and at Windfall bridge some of the SOD rates were slightly negative but stable (Table 6). Thus the SOD rate appeared to be

Table 5. Number of chambers and the date when they were placed *in situ* for each study site on the Athabasca River. The length of time after which DO was measured during an incubation period is also shown for each group of chambers at a study site.

Study Site	Date (d.m.y.)	No. of Chambers		Time (h) DO Measured
		Closed	Open	
Windfall bridge	17.01.90	3	-	24,48,72, and 95
	09.02.90	3	-	42.5
	07.03.90	3	-	43
Whitecourt	16.01.90	3	-	43.5/49.5,67.5, 90.5, and 115
	08.02.90	3	-	44
	06.03.90	3	-	43
Blue Ridge	12.02.90	1	-	44.5
	09.03.90	2	1	42
Fort Assiniboine	10.03.90	3	-	68.5
Smith	12.03.90	3	-	42.5

Table 6. Sediment oxygen demand (SOD) for each chamber and study site on the Athabasca River for different time periods (incubation periods). Mean SOD and coefficient of variation (CV), in parentheses, are also given. Two types of chambers were used, open (O) and closed (C).

Study Site	Date (d.m.y.)	Chamber Type	SOD ($gO_2/m^2/day$) after Incubation period (h)				
			24	42-50	68-72	91-95	115
Windfall bridge	17.01.90*	C	-0.01	0.00	-0.01	0.00	
		C	-0.02	0.00	-0.01	0.00	
		C	---	0.00	0.00	0.00	
	Mean(CV-%)		-0.02(NA)		-0.01(NA)		
	09.02.90	C		0.03			
		C		0.04			
		C		0.03			
	Mean(CV-%)			0.03(17)			
	07.03.90	C		0.01			
		C		0.01			
		C		0.01			
	Mean(CV-%)			0.01(0)			
Whitecourt	16.01.90*	C		---	0.11	0.10	0.09
		C		0.14	0.10	0.10	0.09
		C		0.01	0.01	0.02	0.02
	Mean(CV-%)			0.08(123)	0.07(75)	0.07(63)	0.07(61)
	08.02.90	C		0.47			
		C		0.39			
		C		0.39			
	Mean(CV-%)			0.42(11)			
	06.03.90	C		0.64			
		C		0.66			
		C		0.48			
	Mean(CV-%)			0.59(17)			
Blue Ridge	12.02.90	C		0.06			
	09.03.90	C		0.19			
		C		0.18			
	Mean(CV-%)			0.19(4)			
	09.03.90	O		0.19			
Fort Assiniboine	10.03.90	C			0.08		
		C			0.11		
		C			0.02		
	Mean(CV-%)				0.07(66)		
Smith	12.03.90	C		0.12			
		C		0.06			
		C		0.07			
	Mean(CV-%)			0.08(39)			

* Chambers were left in situ for an extended incubation period

NA CV was not calculated for data with negative values

constant at both sites over a long incubation period. During the incubation period, the greatest decrease in DO concentration in the chambers occurred at Whitecourt (Appendix 1). After 115 h the DO decreased from 10.94 mg/L by an average of 2.44 mg/L in 3 chambers (Appendix 1). This decrease in DO apparently did not inhibit SOD since the SOD rate was stable over the incubation period.

4.2.1.2 Wapiti-Smoky River system

Three closed chambers were left *in situ* in the Wapiti River at Highway 40 for 142.5 h and SOD was measured 3 times (Table 7). A trend in SOD rates at Highway 40 was not clear although SOD did increase slightly after about 48 h during the incubation period (Table 8).

4.2.1.3 Conclusions

In general, the SOD rates were stable or changed by a small amount over the incubation period at the sites examined in 1990. However, for the 1989 study where SOD was measured twice over an incubation period at several sites, there was a general decrease in the SOD rate over time at all sites (except at sites with little SOD, i.e. Windfall bridge). This latter relationship has also been observed by other workers (see Casey and Noton 1989 for references).

To overcome the uncertainty of determining an appropriate incubation period for the 1990 study, the chambers were left *in situ* for the same incubation period, about 48 h (Tables 5 and 7). Thus, with one exception (Fort Assiniboine, 69 h) the SOD rates used in the discussion below were calculated from an

Table 7. Number of chambers and the date when they were placed *in situ* for each study site on the Wapiti-Smoky River system. The length of time after which DO was measured during an incubation period is also shown for each group of chambers at a study site.

Study Site	Date (d.m.y.)	No. of Chambers		Time (h) DO Measured
		Closed	Open	
Wapiti River:				
Hwy. 40	26.01.90	3	-	22.5,46.5, and 142.5
	25.02.90	3	-	42
Downstream of P & G*				
Site 1	22.02.90	3	-	43.5
Site 1	20.03.90	3	-	48.5
Site 2	20.03.90	-	3	47
Mouth	20.03.90	1	-	49
Smoky River:				
Bezanson	26.02.90	2	3	40.5
Watino	23.02.90	3	-	41.5

* Procter and Gamble Cellulose Ltd. mill effluent

Table 8. Sediment oxygen demand (SOD) for each chamber and study site on the Wapiti-Smoky River system for different time periods (incubation periods). Mean SOD and coefficient of variation (CV), in parentheses, are also given. Two types of chambers were used, open (O) and closed (C).

Study Site	Date (d.m.y.)	Chamber Type	SOD ($gO_2/m^2/day$) after Incubation Period (h)		
			22-24	41-49	142.5
Wapiti River:					
Hwy. 40	26.01.90*	C	-0.01	-0.02	0.03
		C	0.02	0.01	0.03
		C	0.00	-0.01	0.03
	Mean(CV-%)		0.00(NA)	-0.01(NA)	0.03(0)
	25.02.90	C		-0.04	
		C		-0.03	
		C		-0.03	
	Mean(CV-%)			-0.03(NA)	
Downstream of P & G**:					
Site 1	22.02.90	C		0.47	
		C		0.29	
		C		0.50	
	Mean(CV-%)			0.42(27)	
Site 1	20.03.90	C		0.17	
		C		0.14	
		C		0.18	
	Mean(CV-%)			0.16(13)	
Site 2	20.03.90	O		0.20	
		O		0.16	
		O		0.17	
	Mean(CV-%)			0.18(12)	
Mouth	20.03.90	C		0.22	
Smoky River:					
Bezanson	26.02.90	C		0.09	
		C		0.04	
	Mean(CV-%)			0.07(54)	
	26.02.90	O		0.07	
		O		0.04	
		O		0.05	
	Mean(CV-%)			0.05(29)	
Watino	23.02.90	C		0.01	
		C		0.01	
		C		0.03	
	Mean(CV-%)			0.02(69)	

* Chambers were left *in situ* for an extended incubation period

** Procter and Gamble Cellulose Ltd. mill effluent

NA CV was not calculated for data with negative values

incubation period of 41-50 h (Tables 6 and 8).

4.2.2 Variation in SOD

Coefficient of variation (CV) was used as a measure of variability for groups of chambers at a site (Tables 6 and 8). The mean CV for the sites on each river system after about 48 h excluding the 'control' sites, were 35% (range = 0-123%, n=8) and 34% (range = 12-69%, n=6) for the Athabasca River and Wapiti-Smoky River system, respectively. These mean CV values were less than the mean CV obtained in 1989 for the Athabasca River (mean CV = 48%, range = 1-140%, n=13) and CV values reported in the literature on SOD. Whittemore (1986) calculated the CV for studies using chambers in situ. For 21 sites, Whittemore found a mean CV = 44% (range = 0-150%, n=61).

4.2.3 Similarity of SOD in open and closed chambers

At Blue Ridge and Bezanson on the Athabasca and Smoky Rivers, respectively, open and closed chambers were used concurrently where fine sediment was abundant. At both sites, the SOD rates were similar in the two types of chambers (Tables 6 and 8). Thus the disturbance to the sediment (which was visibly made up of layers of material e.g., Figure 5) when it was taken from the river bed and placed in the closed chamber did not appear to effect the SOD results.

In 1989 a similar comparison was made between open and closed chambers at Hinton where fine sediment was abundant. Although only one closed chamber was used together with 3 open chambers, the SOD of the closed chamber (0.127

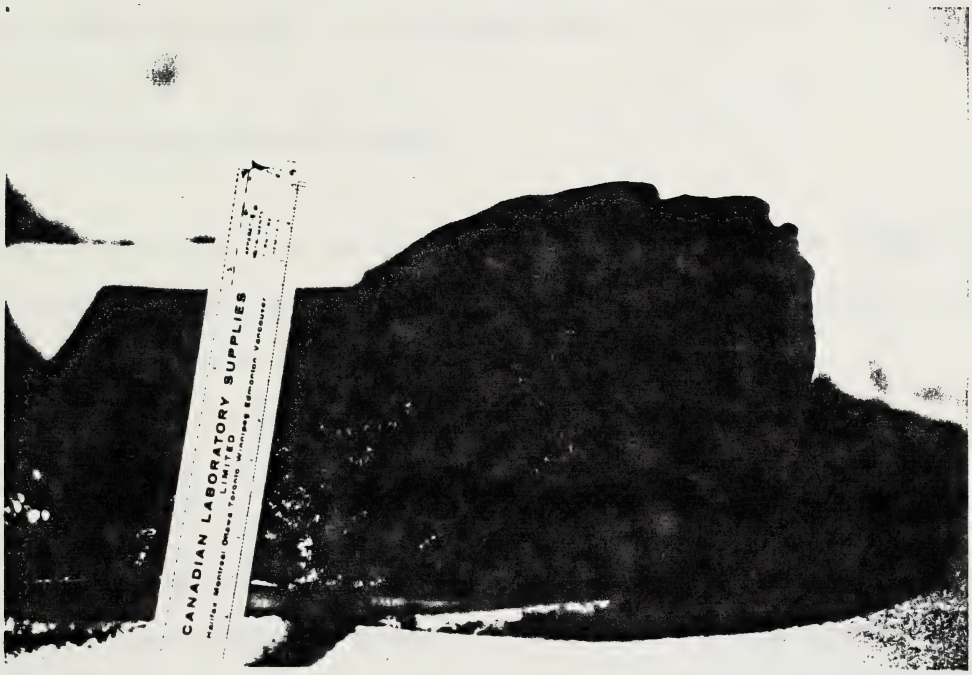

Figure 5. Fine sediment about 2.5 km downstream of the Procter and Gamble Cellulose Ltd. mill (Site 2) on the Wapiti River. The sediment was clearly layered in the undisturbed substratum.

$gO_2/m^2/day$) was equivalent to the SOD in the open chambers (0.116, 0.127 and 0.243 $gO_2/m^2/day$). For a field study with paired samples in a Missouri stream, Hall and Berkas (1988) found that disturbance to the stream bed (gravel and fine sediment) lowered SOD slightly but not significantly.

4.2.4 Change in SOD during the winter

For the Athabasca River and the Wapiti-Smoky River system, an attempt was made to obtain SOD rates at least twice during the winter at a 'control' site and at 1 site immediately downstream of existing pulp mills.

4.2.4.1 Athabasca River

At Windfall bridge, the highest SOD rates were in February and SOD was low in January and March (Table 6, Figure 6). No overall increase or decrease of SOD over winter was evident and the SOD rates were close to zero. The difference between months likely resulted from local variability in stream bed conditions.

At Whitecourt there was an increase in SOD rates over the winter (Table 6, Figure 6). In January at Whitecourt, the site chosen may not have been representative of the river bed substratum. This is because the epilithic growth (which was abundant on the river bed, Figure 7) was only found around the edges of the rocks at this site. At this site, the rocks were probably scraped clean by ice floes. However, from February to March at Whitecourt, there was clearly an increase in the SOD rate Figure 6).

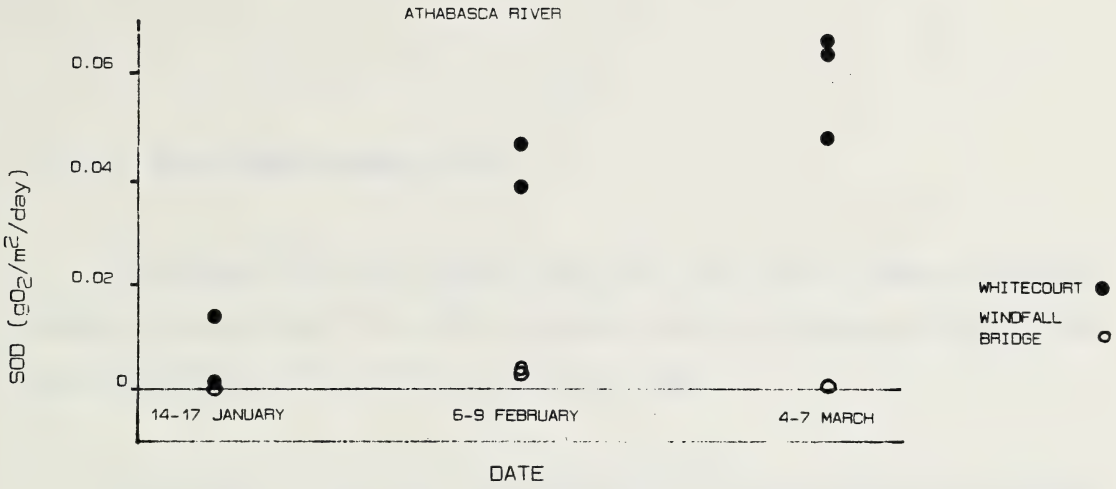

Figure 6. Sediment oxygen demand (SOD) at Whitecourt and Windfall bridge on the Athabasca River during the winter. See section 4.2.4 for details.

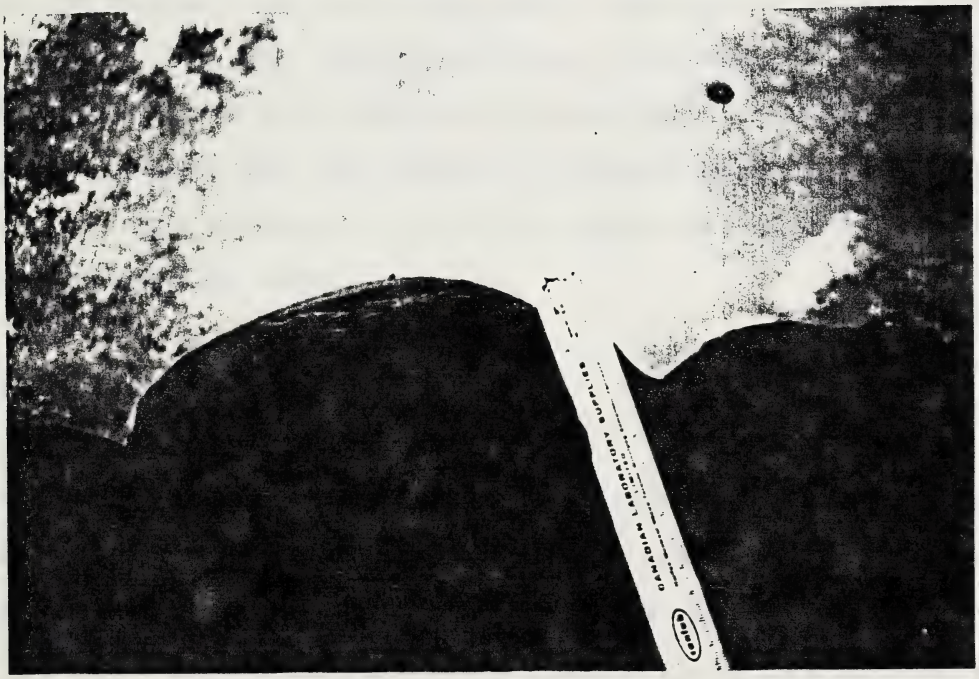

Figure 7. Epilithic growth in March about 1 km downstream of the Millar Western Ltd. pulp mill effluent. At this site algae cover was abundant and up to 1.5 cm thick on most of the river bed.

4.2.4.2 Wapiti-Smoky River system

At Highway 40 on the Wapiti River SOD was lower in February than in January, however, most of the SOD values were negative (Table 8, Figure 8) and no trend in SOD can be determined from the values.

Downstream of the Procter and Gamble mill, the SOD rates for the winter may not be directly comparable. This is because preceeding and during the incubation period in March, the river was rising and flowing very fast, due to melting conditions. This flooding was visibly scouring the epilithic deposits on the rocks and moving the rocks in the river bed. Thus accumulated deposits and organisms causing a SOD may be substantially disturbed and reduced under these conditions. In fact the results obtained for February and March may demonstrate what happens under conditions of spring runoff. The SOD rates were clearly less in March than those obtained in February (Table 8, Figure 8). Although water depth was greater in March, the substratum sampled for SOD was submerged throughout the winter.

4.2.4.3 Conclusions

Results for the Athabasca River suggest that there was a build-up of SOD over the winter downstream of the pulp mill effluent. Using a computer simulation of the oxygen balance in the Athabasca River, Macdonald and Hamilton (1989) postulated that SOD accumulated over the winter in the river in order to explain the observed river oxygen concentrations. The results for the Wapiti-Smoky River system were inconclusive regarding a build-up of SOD over the winter.

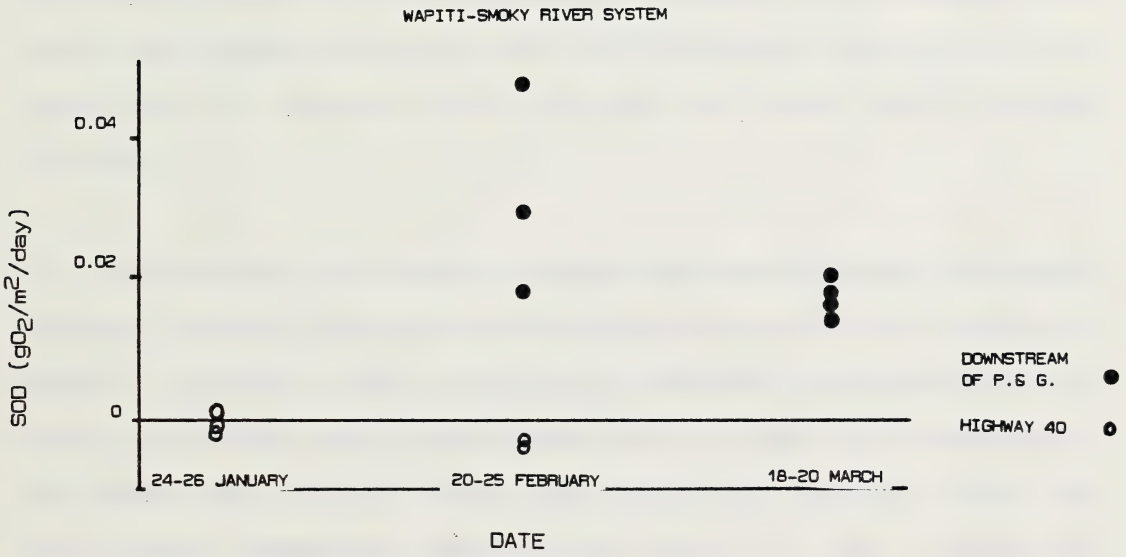

Figure 8. Sediment oxygen demand (SOD)_ downstream of the Procter and Gamble mill and at Highway 40 on the Wapiti-Smoky River system during the winter. See section 4.2.4 for details.

A probable explanation of the 1990 results is the following. Downstream of effluents, nutrient enrichment may have caused increased epilithic growth and biomass of organisms, and increased organic load resulted in an accumulation of organic material over the winter, with low flow and stable river conditions. The principal sources of nutrients and organic material on the Athabasca River and the Wapiti-Smoky River system were the Millar Western and the Procter and Gamble pulp mill effluents and the Whitecourt and Grande Prairie municipal effluents.

Associated with the increase of nutrients and organic material, the benthic community including microorganisms and macroinvertebrates would increase in numbers. For example, such an effect on the zoobenthos has been attributed to organic and nutrient load in the Athabasca River and Wapiti River downstream of the bleached kraft pulp mill effluent and the municipal effluent at Hinton and Grande Prairie, respectively (Anderson 1989, Noton et al. 1989). Although the abundance of the macroinvertebrates were not examined during our study, they are a potentially important factor which may have a significant respiration rate contributing to the SOD (e.g., Bowman and Delfino 1980). Indirectly, macroinvertebrates may also affect SOD by extending the depth of the oxidized layer by disturbing the sediment (Walker and Snodgrass 1986).

The BOD loading of the effluents on these river systems is also most likely very important to the rate of SOD, since the BOD (some of which which settles on the river bed) probably becomes part of the processes contributing to the SOD (also, see 4.2.6.4). Thus SOD of the river bed would be expected to increase

over the winter. But in spring or when the river was flooding much of the epilithic organic material and associated organisms accumulated over winter would be scoured from the river bed and transported downstream. For example, Hall and Berkas (1988) who used chambers in situ in a Missouri stream suggested that scouring of the stream bed during high water may have reduced SOD.

In a study by Edwards and Rolley (1965), the seasonal change in SOD of mud from 2 rivers in the United Kingdom was examined using respirometers at a constant temperature in the laboratory. They conducted their study over a 14 month period; and for both rivers, the minimum and maximum SOD occurred in the winter and spring, respectively. Edwards and Rolley attributed the increase in SOD to the growth of epibenthic algae. For a field study conducted during October in 3 Alaskan streams, Duncan and Brusven (1985) also found a direct relationship between stream productivity and SOD.

4.2.5 SOD of rock and sediment substrata

Downstream of the Procter and Gamble mill, rock and fine sediment were abundant, and closed and open chambers were used for these 2 types of substrata, respectively (Table 8). The rock substrata were found in the main channel of the river and the fine sediment was in a back-water area about 7 m downstream of an ice dam and the railroad trestle (Table 2, Figure 9).

The SOD of the fine sediment (mean = 0.18 $gO_2/m^2/day$) and of the rock substrata (mean = 0.16 $gO_2/m^2/day$) were statistically the same (Mann-Whitney test, p=0.66). However, these SOD rates were measured in March when the river

Figure 9. About 2.5 km downstream of the Procter and Gamble Cellulose Ltd. mill on the Wapiti River. Location of chambers (Site 1) in the main channel and (Site 2) chambers in the back-water downstream of railroad trestle.

was rising and the SOD was most likely reduced especially in the main channel (section 4.2.4.2).

In 1989, the SOD of rock and sediment substrata were measured for one site at Hinton (about 1 km downstream of the combined pulp mill and municipal effluent). At this site the SOD demand was greater for rock substrata than for fine sediment (see Casey and Noton 1989 for further discussion).

4.2.6 Longitudinal trend in SOD rates

To determine the longitudinal trend in SOD along the rivers, SOD was measured for each river system over a period as short as possible in late February and early March.

4.2.6.1 Athabasca River

In March, SOD rates were obtained over an 8 day period from Windfall bridge to the site upstream of Smith (Table 6). Mean SOD clearly increased from 0.01 $gO_2/m^2/day$ at Windfall to 0.59 $gO_2/m^2/day$ at Whitecourt (the highest SOD rate recorded in the 1990 study)(Figure 10). Then, there was a sharp decrease in the SOD downstream to Blue Ridge, Fort Assiniboine and Smith. When all the SOD rates for the Athabasca River over the winter were examined, the same trend was evident, except for the SOD rates obtained in January at Whitecourt (section 4.2.4.1).

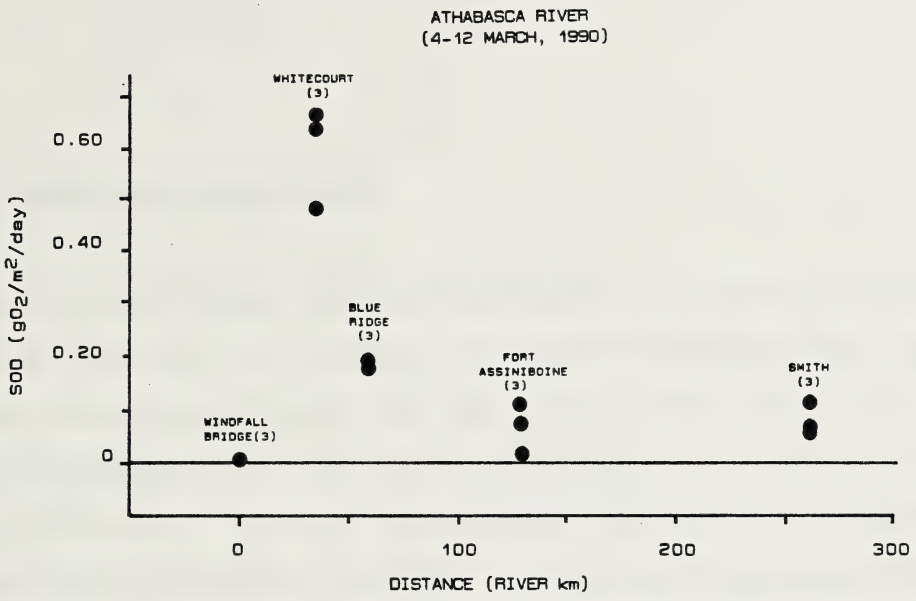

Figure 10. Sediment oxygen demand (SOD) for each study site in March, 1990, on the Athabasca River. The number of readings for each study site are indicated in parentheses.

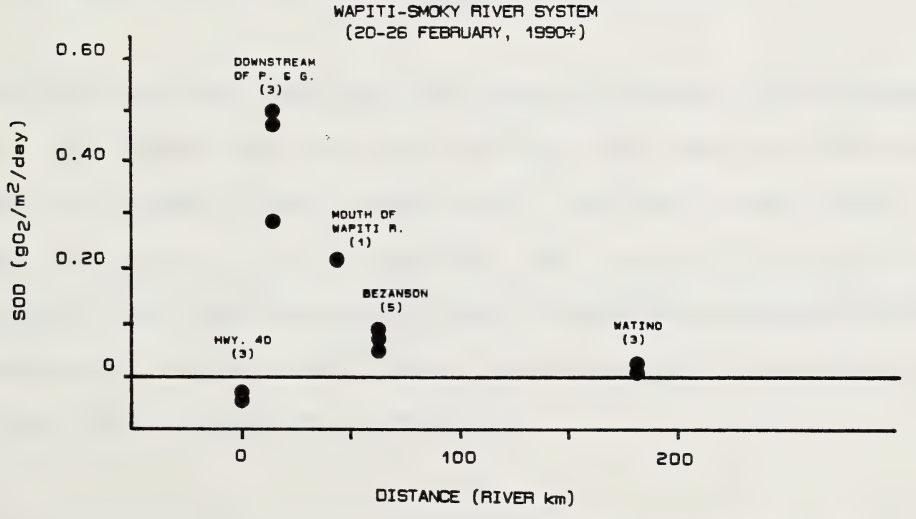

Figure 11. Sediment oxygen demand (SOD) for each study site in February, 1990, on the Wapiti-Smoky River system. The number of readings for each study site are indicated in parentheses. * The SOD rate for the site at the Mouth of the Wapiti River was obtained from 18-20 March.

4.2.6.2 Wapiti-Smoky River system

At the end of February SOD rates were measured at 4 of 5 sites over a 6 day period (Table 8). For the site at the mouth of the Wapiti River, only 1 SOD reading was obtained in March, when the river was rising (section 4.2.4.2). As for the Athabasca River, there was a sharp increase in the SOD rates from Highway 40 (mean SOD = -0.03 $gO_2/m^2/day$) to downstream of the Procter and Gamble mill (mean SOD = 0.42 $gO_2/m^2/day$) and then, a sharp decrease downstream to Watino on the Smoky River (Figure 11). When all the SOD rates for the winter were considered together the same general trend was apparent.

4.2.6.3 Comparison of 1989 and 1990 SOD for Athabasca River

The SOD results for 1989 were very similar to those in 1990 (Figures 10 and 12). The highest and lowest SOD rates for both years were obtained at Whitecourt and Windfall bridge, respectively. The range in mean SOD for 1989 and 1990 was 0.001 to 0.515 $gO_2/m^2/day$ and -0.03 to 0.59 $gO_2/m^2/day$, respectively. Also, the longitudinal trend in SOD on the Athabasca River was the same for both years at Windfall bridge, Whitecourt and Fort Assiniboine (the sites where SOD was measured for both years).

4.2.6.4 Comparison of Athabasca River and Wapiti-Smoky River system

The mean SOD rates were generally greater on the Athabasca River than on the Wapiti-Smoky River system. For the sites downstream of the Millar Western

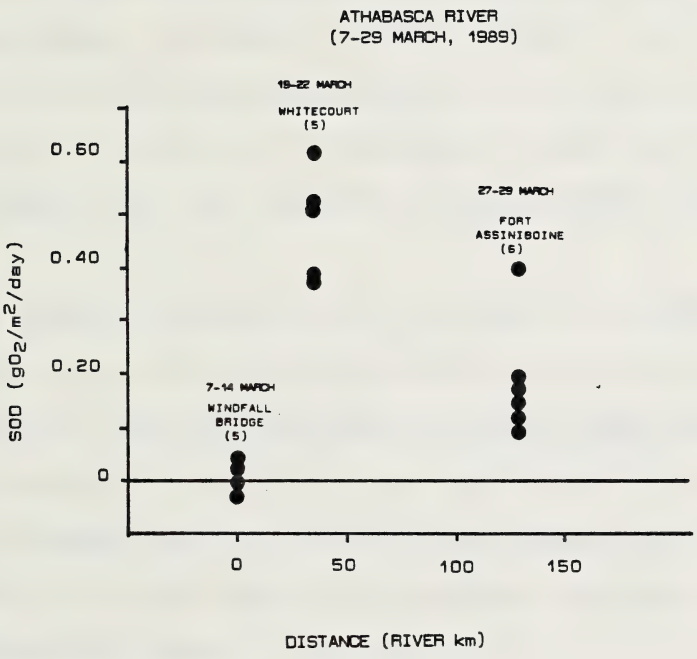

Figure 12. Sediment oxygen demand (SOD) for each study site in 1989 on the Athabasca River. The number of readings for each study site are indicated in parentheses.

mill effluent and of the Procter and Gamble mill effluent, the mean SOD was 0.59 and 0.42 $gO_2/m^2/day$, respectively. Also, for sites furthest downstream of the effluents, the mean SOD was higher on the Athabasca River than on the Wapiti-Smoky River system. For example, at Watino (about 170 km downstream) the mean SOD was 0.02 $gO_2/m^2/day$ and at Smith (about 227 km downstream) the mean SOD was 0.08 $gO_2/m^2/day$. Thus the rate of SOD appeared to remain high further downstream in the Athabasca River when compared to the Wapiti-Smoky system.

The apparent difference in SOD rates between the Athabasca River and the Wapiti-Smoky River system may be due to diferences in the type of pulp mill and the effluents. From the 1990 results it appears that the chemical thermal mechanical pulp (CTMP) mill effluent and the Whitecourt municipal effluent may have had a greater effect on the SOD of the Athabasca River than the bleached kraft pulp mill and the Grande Prairie municipal effluents on the SOD of the Wapiti-Smoky River system.

Also, in 1989 on the Athabasca River, the SOD rates downstream of the Millar Western CTMP mill were greater (mean = 0.515 and 0.457 $gO_2/m^2/day$ during 19-22 March, range=0.386-0.611 $gO_2/m^2/day$) than the SOD rates about 1 km downstream of the bleached kraft pulp mill at Hinton (mean = 0.357, 0.174 and 0.185 $gO_2/m^2/day$ during 19-28 February, range = 0.074-0.435 ($gO_2/m^2/day$) (Casey and Noton 1989). In 1989, the BOD load of the final effluent of the Millar Western mill was about twice that of the final effluent from the Procter and Gamble mill (Noton and Shaw 1989, Noton et al. 1989). However, the BOD loadings for the Millar Western mill were recorded during its first year of operation (January to March, 1989) and the BOD load of the effluent may have been higher

than levels expected under normal operating conditions of the mill. A secondary effluent treatment (activated sludge) system was installed at the Millar Western pulp mill and began operation in December 1989.

In summary, the SOD rates downstream of the combined kraft pulp mill and municipal effluent at Hinton in 1989 were similar to the SOD rates downstream of kraft pulp mill and the Grande Prairie municipal effluent on the Wapiti River. Both of the pulp mills at Hinton and Grande Prairie have secondary effluent treatment (aerated stabilization basin) systems.

4.2.6.5 Percent organic content of epilithic sediment and bottom sediment

4.2.6.5.1 Athabasca River

The percent organic content of the scrapes of the epilithic sediment and SOD in the chambers were not statistically related (Figure 13a). Predictably for the bottom sediment samples, the gravel and sand had a lower percent organic content than the fine sediment samples (Table 9). The regression coefficient for the organic content of the gravel and sand and the SOD rates was negative (Figure 13b). However, the regression coefficient for the percent organic content of the fine sediment and SOD was positive and statistically significant for the sites where fine sediment was abundant, Blue Ridge, Fort Assiniboine, and Smith (Figure 13c).

Table 9. Percent organic content (as percentage of dry weight of sediment) of epilithic sediment and bottom sediment samples in the chambers for each study site and date in the Athabasca River. For the bottom sediment, gravel and sand (G&S) samples were taken from the base of the chambers and fine sediment (FS) samples was taken from the top of the substratum in the chambers.

Study Site	Date (d.m.y.)	Percent Organic Content(%)			
		Epilithic Sediment (10 cm^2)		Bottom Sediment (30 cm^3)	
		Sample	Mean	Sample	Mean
Windfall bridge	11.02.90	0.61 0.80 0.71	0.71	--- --- ---	
	09.03.90	---		1.68(G&S)	---
Whitecourt	10.02.90	1.62 2.37 2.40	2.13	--- --- ---	
	08.03.90	1.31 18.76 1.48	7.18	0.36(G&S) 0.36(G&S) 0.40(G&S)	0.37
Blue Ridge	14.02.90	1.06	---	1.60(G&S)	---
	11.03.90	--- ---		2.26(FS) 2.52(FS)	2.39
	11.03.90	---		2.67(FS)*	
Fort Assiniboine	13.03.90	--- --- ---		2.16(FS) 1.07(FS) 2.65(FS)	1.96
Smith	14.03.90	11.57 2.57	7.07	1.43(FS) 1.63(FS)	1.53
	14.03.90			1.48(G&S)	---

* Open chamber was used instead of a closed chamber

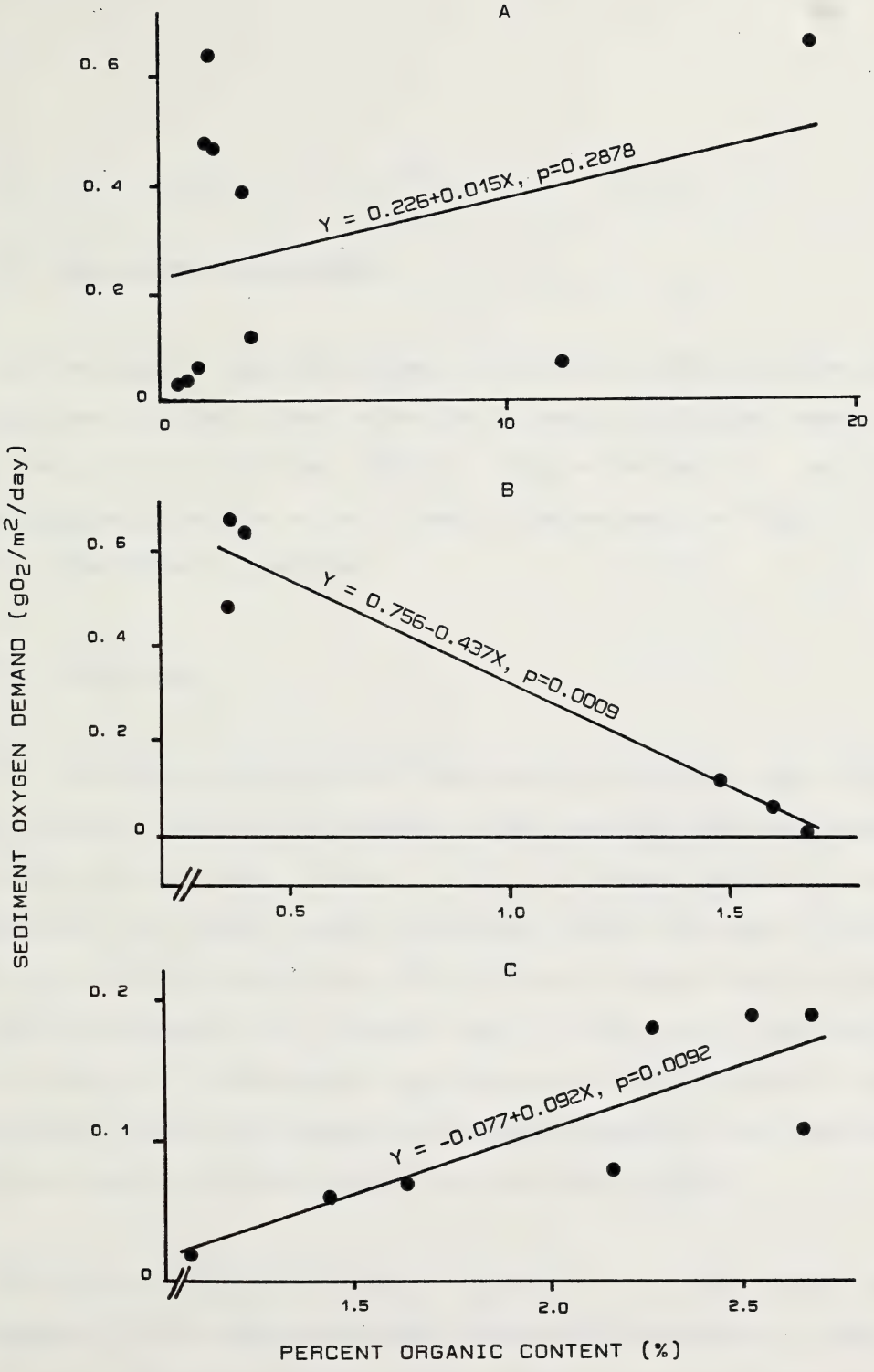

Figure 13. Regression equations for sediment oxygen demand and the percent organic content of scrapes of (A) epilithic sediment and bottom sediment samples of (B) gravel and sand, and (C) fine sediment on the Athabasca River during the winter, 1990. The probability of the regression coefficient being different from zero is also given.

4.2.6.5.2 Wapiti-Smoky River system

For the scrapes of epilithic sediment and the bottom samples of gravel and sand which were obtained at most sites the regression coefficients were not statistically different from zero (Table 10, Figures 14a and 14b). For fine sediment, although the slope of the regression line was positive (Figure 14c), it was not statistically significant.

4.2.6.5.3 Conclusions

For the Athabasca River and the Wapiti-Smoky River system, the percent organic content of the epilithic sediment and the gravel and sand samples were not related to the SOD rates. However, for the fine sediment samples from the Athabasca River, the percent organic content and the SOD rates were directly related. On the Wapiti-Smoky River system the percent organic content and SOD were directly related but the regression was not statistically significant. When the results for the fine sediment and SOD were considered together for the Athabasca River and the Wapiti-Smoky River system the regression coefficient was positive and statistically significant ($Y=-0.062+0.086X$, $p=0.006$)

In a review of SOD model formulas, Porcella et al. (1986) stated that there appeared to be no strong relationship between SOD and measures of organic matter, however, they suggest that this may be due to inaccurate measurement techniques of SOD (e.g., see section 4.2.5 Casey and Noton 1989). In another review, Walker and Snodgrass (1986) concluded that several researchers who used

Table 10. Percent organic content (as percentage of dry weight of sediment) of epilithic sediment and bottom sediment samples in the chambers for each study site and date in the Wapiti-Smoky River system. For the bottom sediment, gravel and sand (G&S) samples were taken from the base of the chambers and fine sediment (PS) samples was taken from the top of the substratum in the chambers.

Study Site	Date (d.m.y.)	Percent Organic Content(%)			
		Epilithic Sediment (10 cm^2)		Bottom Sediment (30 cm^3)	
		Sample	Mean	Sample	Mean
Wapiti River:					
Hwy. 40	01.02.90	--- --- ---		2.31(G&S) 2.34(G&S) 2.75(G&S)	2.47
	27.02.90	4.76	---	1.81(G&S) 1.25(G&S) 1.63(G&S)	1.56
Downstream of P&G*:					
Site 1	24.02.90	5.07 5.10 3.40	4.52	0.78(G&S) 0.93(G&S) 1.06(G&S)	0.92
Site 1	22.03.90	--- --- ---		0.70(G&S) 0.79(G&S) 0.59(G&S)	0.69
Site 2	22.03.90	--- --- ---		2.18(PS)** 1.77(PS)** 1.98(PS)**	1.98
Mouth	22.03.90	5.64	---	---	
Smoky River:					
Bezanson	28.02.90	--- --- ---		1.43(PS)** 1.52(PS)** 1.98(PS)**	1.64
	28.02.90	--- ---		2.50(PS) 1.80(PS)	2.15
Watino	25.02.90	6.69 1.48	4.09	0.42(G&S) 0.43(G&S) 0.39(G&S)	0.41

* Procter and Gamble Cellulose Ltd. mill effluent
** Open chamber used instead of a closed chamber

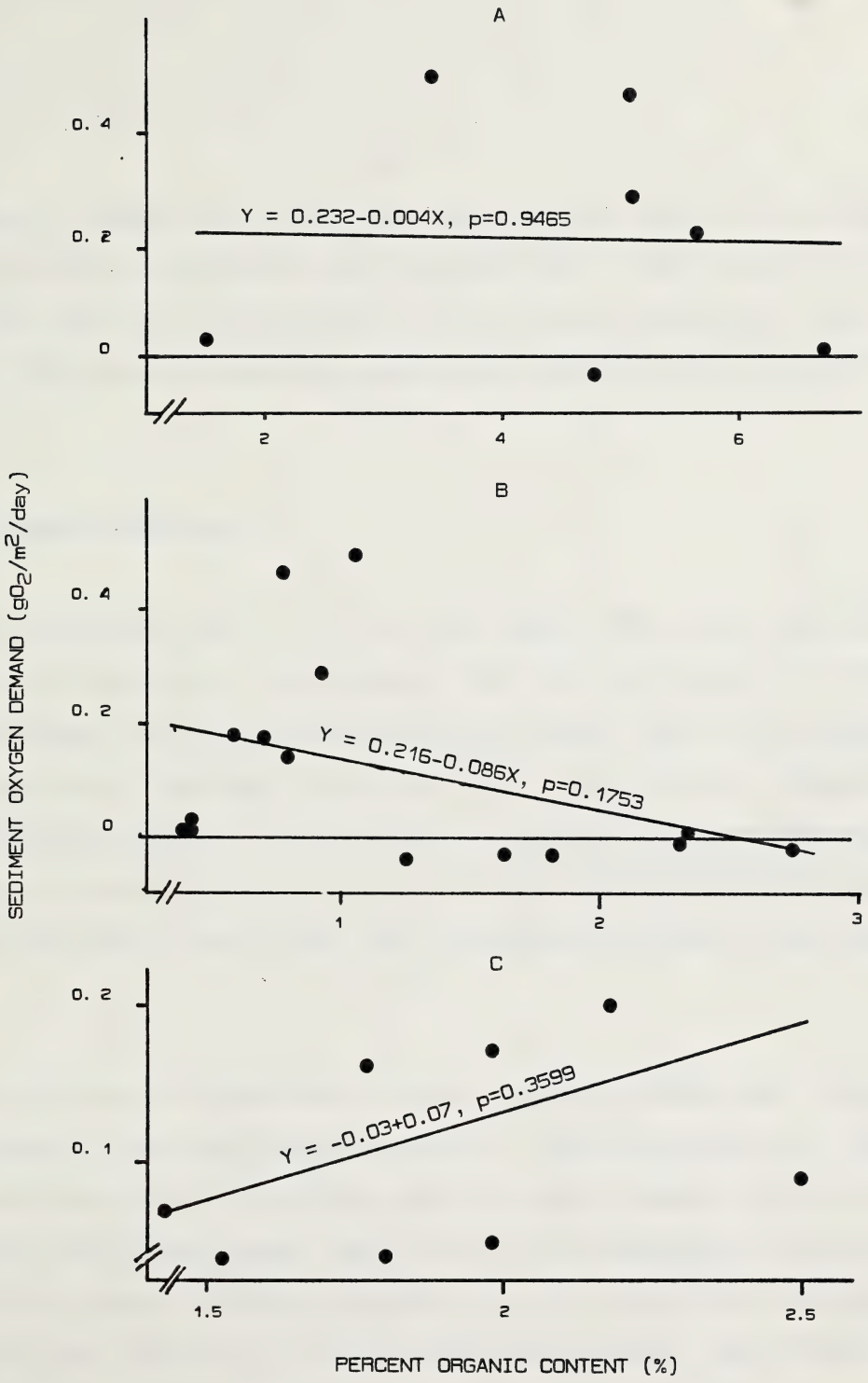

Figure 14. Regression equations for sediment oxygen demand and the percent organic content of scrapes of (A) epilithic sediment and bottom sediment samples of (B) gravel and sand, and (C) fine sediment on the Wapiti-Smoky River system during the winter. The probability of the regression coefficient being different from zero is also given.

measurements of organic matter (including loss on ignition used for this study) have not been able to identify an organic parameter that is best related to SOD. It is likely that due to the complexity of the processess causing SOD it may be difficult to determine a measure of organic matter which is closely related to SOD.

4.2.6.6 General conclusions

The longitudinal trend in SOD rates was similar for both the Athabasca River and the Wapiti-Smoky River system. For both river systems, the SOD increased sharply from very low SOD rates at the 'control' sites to the highest rates immediately downstream of the pulp mill and municipal effluents. Downstream of the effluents, the SOD was shown to decrease sharply and then more gradually for sites most distant from the effluents. For the Athabasca River, the same longitudinal trend in SOD during the winter was evident in 1989 and 1990.

The SOD rates in the Athabasca River were generally greater than the SOD rates measured in the Wapiti-Smoky River system. The Millar Western Ltd. mill and the Whitecourt municipal effluent appeared to have a greater effect on the rate of SOD and the longitudinal trend in SOD in the Athabasca River than the effect of the Procter and Gamble Cellulose Ltd. mill effluent and the Grande Prairie municipal effluent in the Wapiti-Smoky River system. This difference between SOD rates may be due to the type of pulp mill and effluent.

For the Athabasca River and the Wapiti-Smoky River system, evidence was found to indicate that the percent organic content of fine sediment and SOD were directly related. However, the SOD was not directly related to the percent organic content of the epilithic sediment or the gravel and sand bottom samples of the rivers in this study.

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6. APPENDICES

Appendix 1. Dissolved oxygen concentration (DO, mg/L) in the water column and the change in DO for each chamber and study site after the incubation period on the Athabasca River. The types of chambers used were open (O), closed (C), and control (Con).

Study Site / Date (d.m.y.)	Water Column DO (mg/L)	Chamber Type	Decrease in DO (mg/L) in Each Chamber after Incubation Period (h)				
			24	42-50	68-72	91-95	115
Windfall bridge							
17.01.90*	11.09	C	0.10	0.30	0.30	0.49	
		C	0.10	0.20	0.30	0.39	
		C	---	0.25	0.34	0.44	
		Con	+0.20	+0.25	+0.45	+0.50	
09.02.90	10.66	C		0.35			
		C		0.40			
		C		0.30			
		Con		0.05			
07.03.90	10.13	C		0.15			
		C		0.10			
		C		0.10			
		Con		+0.05			
Whitecourt							
16.01.90*	10.94	C		---	2.62	3.17	3.51
		C		1.73	2.18	2.62	2.97
		C		0.24	0.59	0.74	0.84
		Con		+0.15	+0.30	+0.25	+0.30
08.02.90	10.51	C		6.03			
		C		4.28			
		C		4.23			
		Con		0.05			
06.03.90	10.13	C		6.98			
		C		6.69			
		C		4.59			
		Con		0.25			
Blue Ridge							
12.02.90	10.21	C		0.64			
		Con		+0.05			
09.03.90	9.88	C		1.49			
		C		1.39			
		O		1.64			
		Con		+0.05			
Fort Assiniboine							
10.03.90	9.53	C			1.14		
		C			1.44		
		C			0.30		
		Con			0.05		
Smith							
12.03.90	8.54	C		1.35			
		C		0.55			
		C		0.70			
		Con		+0.05			

* Chambers were left in situ for an extended incubation period

Appendix 2. Dissolved oxygen concentration (DO, mg/L) in the water column and the change in DO for each chamber and study site after the incubation period on the Wapiti-Smoky River system. The types of chambers used were open (O), closed (C), and control (Con).

Study Site / Date (d.m.y.)	Water Column DO (mg/L)	Chamber Type	Decrease in DO (mg/L) in Each Chamber after Incubation Period (h)		
			22-24	41-49	142.5
Wapiti River:					
Hwy. 40 *					
26.01.90	11.83	C	0.09	0.19	1.13
		C	0.24	0.39	1.08
		C	0.14	0.29	1.13
		Con	+0.05	+0.35	+0.35
25.02.90	10.96	C		0.00	
		C		+0.05	
		C		+0.05	
		Con		+0.40	
Downstream of P & G**:					
Site 1					
22.02.90	10.07	C		4.46	
		C		2.70	
		C		5.09	
		Con		0.05	
Site 1					
20.03.90	12.08	C		2.00	
		C		1.60	
		C		1.90	
Site 2					
20.03.90		O		2.99	
		O		2.45	
		O		2.65	
		Con		0.10	
Mouth					
20.03.90	12.13	C		2.55	
		Con		0.25	
Smoky River:					
Bezanson					
26.02.90	9.42	C		0.95	
		C		0.60	
		O		1.00	
		O		0.70	
		O		0.85	
		Con		+0.30	
Watino					
23.02.90	8.62	C		0.10	
		C		0.10	
		C		0.20	
		Con		0.00	

* Chambers were left *in situ* for an extended incubation period

** Procter and Gamble Cellulose Ltd. mill effluent

N.L.C. - B.N.C.
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